

Regular article

Deadwood in configuration spaces. II. Singles + doubles and singles + doubles + triples + quadruples spaces

Joseph Ivanic, Klaus Ruedenberg

Ames Laboratory USDOE and Department of Chemistry, Iowa State University, Ames, IA 50011, USA

Received: 14 August 2001 / Accepted: 6 December 2001 / Published online: 8 April 2002
© Springer-Verlag 2002

Abstract. The effect of truncating singles+doubles configuration interaction (CISD) and singles + doubles + triples + quadruples (CISDTQ) spaces on the energies of the systems Ne, H₂O, CO and C₂ is investigated through the use of a previously described, general, selected CI program. CI expansions generated by Hartree–Fock orbitals as well as by natural orbitals are examined and the latter typically exhibit faster convergence as regards the energy. For the CISD wavefunctions of Ne, H₂O, CO and C₂, chemical accuracy is reached by using, respectively, 34, 47, 53 and 55% of the full sets. For the triples + quadruples parts of the wavefunctions on the other hand, chemical accuracy is already reached by using only 1, 4, 6 and 9% of the respective full sets.

Key words: Electron correlation – Configuration interaction

1 Introduction

Full configuration space expansions yield the optimal electronic wavefunctions that can be generated from given orbital bases through determinantal construction and they also avoid any bias that can result from arbitrary configuration choices; however, they not only grow exceedingly rapidly with the size of the orbital spaces, but they also contain large numbers of configurations that are useless for generating electronic wavefunctions. This is particularly so when large full-space expansions are used for the recovery of dynamic correlations. It is therefore of interest to have some benchmark investigations that systematically identify the amount of such “deadwood” and “live wood” in an unbiased manner for some prototype systems. In a previous investigation, [1] we did this for the full configuration interaction (CI) spaces of several mole-

cules by solving the CI problems for a series of truncated CI expansions. We documented that, at the level of chemical accuracy (1 mhartree), the live wood contributed less than 1% of the full configuration spaces.

Since, for systems dominated by one determinant, configurational expansions are known to converge rapidly with respect to the excitation level, i.e. singles+doubles (SD) CI, singles + doubles + triples + quadruples (SDTQ) CI, etc. [2], most of the deadwood in large spaces used for dynamical correlations comes from the higher excitations. In the present investigation, we address, therefore, the question how much deadwood and live wood is carried along in the SD parts and in the TQ parts of the full CI wavefunctions of the systems examined in the previous investigation, [1] viz. Ne, H₂O, CO, C₂ containing up to 450,000 determinants. For a 4,120-dimensional SD excitation space of the water ground state, Shavitt et al. [3] analyzed this problem in 1976 and, as regards SDTQ wavefunctions, relevant expectations can be inferred from the various schemes for generating CI expansions by means of successive multireference SD-CI calculations. [4] The results reported here complement this previous information. Our approach is, however, strictly analytical. We first determine the exact SD/SDTQ wavefunctions and then generate from them natural-orbital (NO)-based sequences of truncated expansions in the order of most rapid convergence. Thereby, we obtain a measure of the amount of necessary live wood and we trace this as a function of the achieved accuracy in the energy. We are not aware of a prior systematic documentation of this quantitative dependence.

2 Method

SD and SDTQ expansions

The CISD and the CISDTQ wavefunctions are given by [5]

$$\Psi_{\text{SD}} = C_{\text{Ref}} \Psi_{\text{Ref}} + \sum_i^{\text{occ vir}} \sum_m C_i^m \Psi_i^m + \sum_{i < j}^{\text{occ vir}} \sum_{m < n} C_{ij}^{mn} \Psi_{ij}^{mn}, \quad (1)$$

Table 1. Contribution to the singles + doubles configuration interaction (*CISD*) energy of truncated spaces for Ne (basis set from Ref. [6])

Orbital set ^a	No. of determinants	Percentage space ^b	$E_{TCl}-E_{SCF}^c$	$E_{CISD}-E_{TCl}^c$	% E_{CORR}^d
Fock virtual orbitals	40	4.66	-0.09887912	-0.08899920	52.629
	71	8.28	-0.14352310	-0.04435522	76.392
	141	16.43	-0.17065689	-0.01722143	90.834
	291	33.92	-0.18342114	-0.00445718	97.628
	342	39.86	-0.18488467	-0.00299365	98.407
	465	54.20	-0.18608610	-0.00179222	99.046
	558	65.03	-0.18760380	-0.00027452	99.854
	635	74.01	-0.18785458	-0.00002374	99.987
	751	87.53	-0.18787779	-0.00000054	~100
Virtual natural orbitals	40	4.66	-0.10492721	-0.08295111	55.848
	64	7.46	-0.14328130	-0.04459702	76.263
	130	15.15	-0.17639675	-0.01148157	93.889
	231	26.92	-0.18555187	-0.00232645	98.762
	351	40.91	-0.18754591	-0.00033241	99.823
	517	60.26	-0.18779332	-0.00008500	99.955
	578	67.37	-0.18783635	-0.00004197	99.978
	665	77.51	-0.18786518	-0.00001314	99.993
	745	86.83	-0.18787779	-0.00000053	~100

^a Correlating orbitals. Fock virtual = virtual eigenfunctions of Fock operator. Virtual natural orbitals = eigenfunctions of first-order density block in the virtual space of the full-space CI calculation

^b Percentage of SD determinants taken in the truncated CI

^c E_{TCl} = energy of truncated CI. Energies in hartree

^d % $E_{CORR} = [(E_{TCl}-E_{SCF})/(E_{CISD}-E_{SCF})] \times 100$

Table 2. Contribution to the singles + doubles + triples + quadruples CI (*CISDTQ*) energy of truncated spaces for Ne (basis set from Ref. [6])

Orbital set ^a	No. of determinants	Percentage space ^b	$E_{TCl}-E_{SCF}^c$	$E_{CISDTQ}-E_{TCl}^c$	% E_{CORR}^d
Fock virtual orbitals	675	0.49	-0.18944186	-0.00397210	97.946
	1,836	1.33	-0.19172304	-0.00169092	99.126
	5,537	4.00	-0.19276744	-0.00064651	99.666
	10,731	7.76	-0.19314937	-0.00026459	99.863
	20,092	14.53	-0.19332672	-0.00008724	99.955
	36,103	26.11	-0.19339651	-0.00001744	99.991
	62,893	45.48	-0.19341267	-0.00000129	99.999
	106,178	76.79	-0.19341395	-0.00000001	~100
	128,908	93.23	-0.19341396	~0	~100
	Virtual natural orbitals	713	0.52	-0.19129219	-0.00212176
1,969		1.42	-0.19231902	-0.00109494	99.434
5,522		3.99	-0.19308318	-0.00033077	99.829
9,142		6.61	-0.19330644	-0.00010752	99.944
16,220		11.73	-0.19338660	-0.00002735	99.986
33,728		24.39	-0.19341089	-0.00000306	99.998
64,736		46.82	-0.19341368	-0.00000027	~100
104,678		75.70	-0.19341395	-0.00000001	~100
129,688		93.79	-0.19341396	~0	~100

^a Correlating orbitals. Fock virtual = virtual eigenfunctions of Fock operator. Virtual natural orbitals = eigenfunctions of first-order density block in the virtual space of the full-space CI calculation

^b Percentage of SDTQ determinants taken in the truncated CI

^c E_{TCl} = energy of truncated CI Energies in hartree

^d % $E_{CORR} = [(E_{TCl}-E_{SCF})/(E_{CISDTQ}-E_{SCF})] \times 100$

$$\Psi_{SDTQ} = \hat{C}_{Ref} \Psi_{Ref} + \sum_i^{occ} \sum_m^{vir} \hat{C}_i^m \Psi_i^m + \sum_{i<j}^{vir} \sum_{m<n}^{vir} \hat{C}_{ij}^{mn} \Psi_{ij}^{mn} + \sum_{i<j<k}^{occ} \sum_{m<n<o}^{vir} \hat{C}_{ijk}^{mno} \Psi_{ijk}^{mno} + \sum_{i<j<k<l}^{occ} \sum_{m<n<o<p}^{vir} \hat{C}_{ijkl}^{mnop} \Psi_{ijkl}^{mnop}, \quad (2)$$

where the reference function Ψ_{Ref} is a single self-consistent-field (SCF) determinant in the cases considered here. The abbreviation occ refers to the spin orbitals that are occupied in Ψ_{Ref} and denoted by subscripts, whereas vir refers to a set of virtual orbitals that are unoccupied in Ψ_{Ref} and denoted by superscripts. Moreover, Ψ_{ij}^{mn}

signifies a determinant obtained by replacing the spin orbitals χ_i, χ_j in Ψ_{Ref} by the virtual spin orbitals χ_m, χ_n , etc. Corresponding coefficients for the two approximations (Eqs. 1, 2) differ of course somewhat, as determined by the two energy minimizations.

In the examination of CO and C₂, the inner-shell core orbitals were kept doubly occupied in all determinants so that the summations over i,j,k,l do not include these orbitals. Furthermore, the highest virtual orbital was not used for C₂ so that, in that case, the summations over m,n,o,p do not include this orbital. For Ne and H₂O, all orbitals, including the core, were included in the CI calculations.

Table 3. Contribution to the CISD energy of truncated spaces for H₂O (basis set from Ref. [7])

Orbital set ^a	No. of determinants	Percentage space ^b	$E_{\text{TCI}}-E_{\text{SCF}}^c$	$E_{\text{CISD}}-E_{\text{TCI}}^c$	% E_{CORR}^d
Fock virtual orbitals	39	4.43	-0.06286686	-0.07598433	45.276
	99	11.25	-0.09210775	-0.04674344	66.336
	166	18.86	-0.11140913	-0.02744206	80.236
	245	27.84	-0.13121707	-0.00763412	94.502
	338	38.41	-0.13590210	-0.00294909	97.876
	435	49.43	-0.13812442	-0.00072678	99.477
	588	66.82	-0.13862842	-0.00022278	99.840
	694	78.86	-0.13878849	-0.00006270	99.955
	815	92.61	-0.13884622	-0.00000497	99.996
	Virtual natural orbitals	34	3.86	-0.08158888	-0.05726231
77		8.75	-0.11062757	-0.02822362	79.673
120		13.64	-0.12776835	-0.01108284	92.018
247		28.07	-0.13416453	-0.00468667	96.625
348		39.55	-0.13671344	-0.00213775	98.460
453		51.48	-0.13820046	-0.00065073	99.531
613		69.66	-0.13866995	-0.00018124	99.869
708		80.45	-0.13880459	-0.00004660	99.966
797		90.57	-0.13884369	-0.00000751	99.995

a,b,c,d See Table 1

Table 4. Contribution to the CISDTQ energy of truncated spaces for H₂O (basis set from Ref. [7])

Orbital set ^a	No. of determinants	Percentage space ^b	$E_{\text{TCI}}-E_{\text{SCF}}^c$	$E_{\text{CISDTQ}}-E_{\text{TCI}}^c$	% E_{CORR}^d
Fock virtual orbitals	816	1.33	-0.13997312	-0.00625230	95.724
	2,275	3.71	-0.14295104	-0.00327438	97.761
	4,639	7.57	-0.14454921	-0.00167621	98.854
	7,540	12.30	-0.14557373	-0.00065169	99.554
	11,369	18.54	-0.14603663	-0.00018879	99.871
	17,313	28.23	-0.14616372	-0.00006170	99.958
	33,625	54.84	-0.14621622	-0.00000920	99.994
	46,682	76.13	-0.14622425	-0.00000117	99.999
	53,603	87.42	-0.14622528	-0.00000014	~100
	Virtual natural orbitals	694	1.13	-0.14217479	-0.00405063
1,780		2.90	-0.14439379	-0.00183163	98.747
3,463		5.65	-0.14541097	-0.00081445	99.443
6,453		10.52	-0.14591789	-0.00030753	99.790
12,274		20.02	-0.14614602	-0.00007940	99.946
18,974		30.94	-0.14620014	-0.00002528	99.983
31,027		50.60	-0.14622095	-0.00000447	99.997
44,677		72.86	-0.14622484	-0.00000058	~100
53,809		87.75	-0.14622536	-0.00000006	~100

a,b,c,d See Table 2

Table 5. Contribution to the CISD energy of truncated spaces for CO (basis set from Ref. [7])

Orbital set ^a	No. of determinants	Percentage space ^b	$E_{\text{TCI}}-E_{\text{SCF}}^c$	$E_{\text{CISD}}-E_{\text{TCI}}^c$	% E_{CORR}^d	
Fock virtual orbitals	58	3.28	-0.09615854	-0.09290874	50.859	
	158	8.96	-0.13392869	-0.05513860	70.837	
	331	18.76	-0.16554313	-0.02352416	87.558	
	568	32.20	-0.18138588	-0.00768140	95.937	
	748	42.40	-0.18614361	-0.00292367	98.454	
	940	53.29	-0.18814968	-0.00091760	99.515	
	1,103	62.53	-0.18871623	-0.00035106	99.815	
	1,291	73.19	-0.18901037	-0.00005692	99.970	
	1,499	84.98	-0.18906243	-0.00000485	99.997	
	Virtual natural orbitals	62	3.51	-0.12361701	-0.06545027	65.383
		144	8.16	-0.15851324	-0.03055404	83.840
		308	17.46	-0.17567526	-0.01339202	92.917
552		31.29	-0.18506226	-0.00400503	97.882	
740		41.95	-0.18762280	-0.00144448	99.236	
950		53.85	-0.18864658	-0.00042070	99.777	
1,104		62.59	-0.18887287	-0.00019441	99.897	
1,271		72.05	-0.18902296	-0.00004433	99.977	
1,501		85.09	-0.18906028	-0.00000700	99.996	

a,b,c,d See Table 1

Table 6. Contribution to the CISDTQ energy of truncated spaces for CO (basis set from Ref. [7])

Orbital set ^a	No. of determinants	Percentage space ^b	$E_{\text{TCI}}-E_{\text{SCF}}^c$	$E_{\text{CISDTQ}}-E_{\text{TCI}}^c$	% E_{CORR}^d
Fock virtual orbitals	1,228	0.44	-0.19363038	-0.01537906	92.642
	3,405	1.23	-0.19983833	-0.00917112	95.612
	12,065	4.37	-0.20483889	-0.00417055	98.005
	25,346	9.17	-0.20709841	-0.00191103	99.086
	48,883	17.69	-0.20833857	-0.00067087	99.679
	81,334	29.45	-0.20884916	-0.00016028	99.923
	119,301	43.18	-0.20897764	-0.00003180	99.985
	193,255	69.94	-0.20900880	-0.00000064	~100
	239,271	86.60	-0.20900942	-0.00000002	~100
Virtual natural orbitals	1,467	0.53	-0.19963442	-0.00937502	95.515
	3,725	1.35	-0.20408269	-0.00492675	97.643
	10,770	3.90	-0.20711264	-0.00189680	99.092
	22,079	7.99	-0.20822945	-0.00077999	99.627
	39,773	14.39	-0.20874433	-0.00026511	99.873
	73,227	26.50	-0.20895201	-0.00005743	99.973
	118,775	42.99	-0.20900078	-0.00000866	99.996
	191,864	69.44	-0.20900918	-0.00000026	~100
	244,021	88.32	-0.20900943	-0.00000001	~100

a,b,c,d See Table 2

Table 7. Contribution to the CISD energy of truncated spaces for C₂ (basis set from Ref. [7])

Orbital set ^a	No. of determinants	Percentage space ^b	$E_{\text{TCI}}-E_{\text{SCF}}^c$	$E_{\text{CISD}}-E_{\text{TCI}}^c$	% E_{CORR}^d
Fock virtual orbitals	64	4.08	-0.16712868	-0.10863996	60.605
	172	10.96	-0.20278225	-0.07298639	73.533
	317	20.20	-0.23163750	-0.04413114	83.997
	578	36.84	-0.25415523	-0.02161342	92.162
	801	51.05	-0.26756741	-0.00820124	97.026
	985	62.78	-0.27291339	-0.00285525	98.965
	1,184	75.46	-0.27526228	-0.00050637	99.816
	1,287	82.03	-0.27563358	-0.00013507	99.951
	1,335	85.09	-0.27572748	-0.00004116	99.985
	Virtual natural orbitals	54	3.44	-0.19497193	-0.08079672
164		10.45	-0.23309894	-0.04266971	84.527
295		18.80	-0.25359711	-0.02217153	91.960
519		33.08	-0.26897807	-0.00679058	97.538
767		48.88	-0.27411541	-0.00165323	99.400
984		62.72	-0.27531445	-0.00045419	99.835
1,140		72.66	-0.27561593	-0.00015271	99.945
1,245		79.35	-0.27571826	-0.00005039	99.982
1,379		87.89	-0.27575968	-0.00000897	99.997

a,b,c,d See Table 1

Truncation of expansions

After obtaining the CISD or CISDTQ wavefunction for a specific system, we rank all determinants according to the absolute values of their CI coefficients in the respective expansions. We then choose the X most important determinants and add to them the least number of determinants required to ensure that the determinant set spans a (reducible) representation of the symmetric group, thereby guaranteeing that the CI solutions of the truncated space will be eigenfunctions of the total spin. The CI coefficients and energies are then determined for an appropriately chosen sequence of X values.

Molecular orbitals

There exists some freedom in the choice of the molecular orbitals (MOs) in the CI calculations, be they of the SD or the SDTQ type. The simplest choice is to use directly the eigenfunctions of the Fock-SCF operator, the occupied SCF-MOs for the reference determinant and the virtual MOs ("Fock virtual MOs") for the correlating determinants. Another choice is to use the same reference MOs, but to construct the correlating determinants from the virtual NOs (VNOs), which are obtained by diagonalizing the first-order density matrix block obtained for the virtual space in the full CI

calculation with all active Fock MOs. We examined the truncations for both correlation orbital choices for all four systems. While the total wavefunctions and energies obtained for a given problem with the two orbital choices are, of course, identical, this is manifestly no longer so for the wavefunctions generated by truncation to a certain number, X , of determinants in the respective orbitals. One would conjecture the energies obtained with the second orbital choice to approach more quickly the energies obtained with all determinants and this expectation is by and large born out by the results reported in the next section.

Alternatively, one can generate the NOs of the total density matrix of the full CI wavefunction obtained with all active Fock orbitals and, then, form a reference determinant from the principal NOs (which have occupations close to 2), and use the secondary NOs as correlating orbitals. We have done this, too, for all four systems. The SD and SDTQ approximations generated in this way approach the full-space energies more slowly than the corresponding aforementioned wavefunctions, although the differences drop below 1 mhartree at the SDTQ level. While it would be of some interest to see whether there is a significant difference in the convergence when these expansions are truncated, we have not examined such truncations.

Table 8. Contribution to the CISDTQ energy of truncated spaces for C_2 (basis set from Ref. [7])

Orbital set ^a	No. of determinants	Percentage space ^b	$E_{TCI}-E_{SCF}^c$	$E_{CISDTQ}-E_{TCI}^c$	% E_{CORR}^d
Fock virtual orbitals	3,066	0.62	-0.31138616	-0.02160470	93.512
	6,909	1.41	-0.31932459	-0.01366627	95.896
	20,477	4.16	-0.32625855	-0.00673231	97.978
	39,684	8.08	-0.32949112	-0.00349974	98.949
	78,759	16.03	-0.33153969	-0.00145117	99.564
	149,187	30.36	-0.33253746	-0.00045340	99.864
	259,280	52.77	-0.33291463	-0.00007623	99.977
	391,866	79.76	-0.33298816	-0.00000271	99.999
	450,275	91.64	-0.33299076	-0.00000010	~100
Virtual natural orbitals	3,324	0.68	-0.31985034	-0.01314052	96.054
	7,208	1.47	-0.32559583	-0.00739503	97.779
	18,388	3.74	-0.33011101	-0.00287985	99.135
	36,867	7.50	-0.33170685	-0.00128401	99.614
	72,851	14.83	-0.33253874	-0.00045212	99.864
	138,184	28.12	-0.33287293	-0.00011793	99.965
	247,160	50.30	-0.33297476	-0.00001610	99.995
	385,238	78.41	-0.33299030	-0.00000056	~100
	452,390	92.07	-0.33299084	-0.00000002	~100track

^{a,b,c,d} See Table 2

Table 9. Convergence analysis of configuration interaction in Ne (basis set from Ref. [6])

cc-pVDZ + [18, 0, 0] ^a	S + D	T + Q ^b	EX > 4	Full [1]
Contribution of various excitation levels				
Number of determinants	858	137,414	9,047,008	9,185,280
Percentage of determinants of full space	0.009	1.496	98.495	100
ΔE_{CORR} (hartree) ^c	-0.18787832	-0.00553563	-0.00012671	-0.19354066
ΔE_{CORR} (% of full) ^c	97.074	2.860	0.065	100
ΔE_{CORR} (hartree) ^d	-0.18773182	-0.00567193	-0.00013692	-0.19354066
ΔE_{CORR} (% of full) ^d	96.999	2.931	0.071	100
Required for mhartree accuracy				
Number of determinants ^c	500	3,409		
Percentage in excitation group ^c	58	2		
Number of determinants ^e	294	1,905		2,245 ^d
Percentage in excitation group ^e	34	1		0.02 ^d
Required for 0.1 mhartree accuracy				
Number of determinants ^c	592	18,463		
Percentage in excitation group ^c	69	13		
Number of determinants ^e	491	8,792		11,683 ^d
Percentage in excitation group ^e	57	6		0.13 ^d

^a Total number of orbitals, number of inactive core orbitals, number of omitted highest orbitals

^b Number of determinants and ΔE = differences (S + D + T + Q) values minus (S + D) values

^c Reference determinant = Fock-SCF orbitals, correlating orbitals = virtual Fock-SCF orbitals

^d Reference determinant in terms of principal natural orbitals of total CI space, correlating orbitals = secondary natural orbitals of total CI space

^e Reference determinant = SCF orbitals, correlating orbitals = natural orbitals in virtual Fock-SCF space

Execution

We have studied the molecules Ne, H₂O, CO, and C₂ using the cc-pVDZ + [6], DZ [7], DZ [7] and DZP [7] basis sets, respectively. They are the same basis sets we used in the previous investigation, where we examined the effects of truncating the full configuration spaces of these systems. They were also used in previous benchmark calculations by other authors. It can be argued that these basis sets recover the essence of the nondynamic correlation energy which is of particular interest to us.

The calculations were performed using our general configuration interaction (GCI) code contained in the JAKAL program set which has been incorporated in the GAMESS program system maintained by M.S. Gordon and M.W. Schmidt [8]. It is a direct CI method capable of determining CI expansions based on arbitrary determinantal configuration lists. For each of the aforementioned calculations, a truncated determinant set is selected and a corre-

sponding integer list submitted as input. The additional determinants, which are required for spin consistency, are automatically generated and included by the program before diagonalizing the Hamiltonian matrix. Details are described in the previous investigation [1].

3 Results

Description of tables

The energy losses resulting from truncating the various expansions using the Fock-SCF determinant as a reference are documented in Tables 1, 2, 3, 4, 5, 6, 7 and 8. In each table, the entries in the first nine rows

Table 10. Convergence analysis of configuration interaction in H₂O (basis set from Ref [7])

DZ [14, 0, 0] ^a	S + D	T + Q ^b	EX > 4	Full [1]
Contribution of various excitation levels				
Number of determinants	880	60,438	941,390	1,002,708
Percentage of determinants of full space	0.088	6.027	93.885	100
ΔE_{CORR} (hartree) ^c	-0.13885119	-0.00737423	-0.00022910	-0.14645452
ΔE_{CORR} (% of full) ^c	94.808	5.035	0.156	100
ΔE_{CORR} (hartree) ^d	-0.13861727	-0.00758695	-0.00025030	-0.14645452
ΔE_{CORR} (% of full) ^d	94.649	5.180	0.171	100
Required for mhartree accuracy				
Number of determinants ^c	410	5,722		
Percentage in excitation group ^c	46	9		
Number of determinants ^e	414	2,619		3,455 ^d
Percentage in excitation group ^e	47	4		0.34 ^d
Required for 0.1 mhartree accuracy				
Number of determinants ^c	667	13,471		
Percentage in excitation group ^c	76	22		
Number of determinants ^e	657	11,267		19,264 ^d
Percentage in excitation group ^e	75	18		1.92 ^d

a,b,c,d,e See Table 9

Table 11. Convergence analysis of configuration interaction in CO (basis set from Ref [7])

DZ [20, 2, 0] ^a	S + D	T + Q ^b	EX > 4	Full [1]
Contribution of various excitation levels				
Number of determinants	1,764	274,542	18,091,246	18,367,552
Percentage of determinants of full space	0.010	1.495	98.496	100
ΔE_{CORR} (hartree) ^c	-0.18906728	-0.01994216	-0.00136258	-0.21037202
ΔE_{CORR} (% of full) ^c	89.873	9.479	0.648	100
ΔE_{CORR} (hartree) ^d	-0.18761477	-0.02123810	-0.00151915	-0.21037202
ΔE_{CORR} (% of full) ^d	89.182	10.095	0.722	100
Required for mhartree accuracy				
Number of determinants ^c	929	38,125		
Percentage in excitation group ^c	53	14		
Number of determinants ^e	810	17,741		25,025 ^d
Percentage in excitation group ^e	46	6		0.14 ^d
Required for 0.1 mhartree accuracy				
Number of determinants ^c	1,234	93,472		
Percentage in excitation group ^c	70	34		
No. of determinants ^e	1,141	61,510		149,451 ^d
Percentage in excitation group ^e	65	22		0.81 ^d

a,b,c,d,e See Table 9

contain the results obtained using the Fock virtual orbitals and those in the last nine rows contain the results obtained using the VNOs. The first data column lists the number of determinants in the truncated expansions and the second column expresses this number as the percentage of the total number of determinants possible at the excitation level considered. The third and fourth data columns list the correlation energies recovered and not recovered, respectively, by the various truncated expansions so that, for each row, the sum of these two columns adds up to the total correlation energy recovered at the excitation level considered (SD or SDTQ). The last column gives the percentages of this total that are recovered by the truncated expansions as given in the third column.

Some quantitative inferences that can be drawn from the raw data in the preceding tables are provided in

Tables 9, 10, 11 and 12. The data columns of the first sections of Tables 9, 10, 11 and 12 furnish a comparison of the importance of the excitation levels SD, SDTQ and excitation above level 4 to the results of the full CI space. Specifically, the determinant numbers and the energies listed in the T+Q column are (T + Q) contributions defined as the differences between the SDTQ and the SD calculations. The first row lists the number of determinants and the second row expresses this number as a percentage of the dimension of the full space. The third row lists the correlation energies recovered when the Fock-SCF orbitals are used and the next row expresses these as percentages of the correlation energies recovered in the full CI space. The fifth and sixth columns list the analogous results obtained when the NOs of the total density matrix of the full CI calculation are used, as discussed previously.

The second and third sections of Tables 9, 10, 11 and 12 exhibit the lengths of the truncated expansions that are required at each excitation level to recover the correlation energy achievable at that excitation level to an accuracy of 1 and 0.1 mhartree, respectively. In each of

these two sections, the first row lists the number of determinants required when the Fock-SCF MOs are used for reference and correlation orbitals, and the second row expresses this number as a percentage of the total number of determinants possible at that excitation level

Table 12. Convergence analysis of configuration interaction in C_2 (basis set from Ref [7])

DZP [30, 2, 1] ^a	S + D	T + Q ^b	EX > 4	Full [1]
Contribution of various excitation levels				
Number of determinants	1,569	489,762	38,013,817	38,505,148
Percentage of determinants of full space	0.004	1.272	98.724	100
ΔE_{CORR} (hartree) ^c	-0.27576864	-0.05722222	-0.00654106	-0.33953192
ΔE_{CORR} (% of full) ^c	81.220	16.853	1.926	100
ΔE_{CORR} (hartree) ^d	-0.27143846	-0.06080387	-0.00728959	-0.33953192
ΔE_{CORR} (% of full) ^d	79.945	17.908	2.147	100
Required for mhartree accuracy				
Number of determinants ^e	1,120	101,313		
Percentage in excitation group ^c	71	21		
Number of determinants ^e	865	44,275		104,317 ^d
Percentage in excitation group ^e	55	9		0.27 ^d
Required for 0.1 mhartree accuracy				
Number of determinants ^c	1,303	240,460		
Percentage in excitation group ^c	83	49		
Number of determinants ^e	1,181	153,337		739,299 ^d
Percentage in excitation group ^e	75	31		1.92 ^d

a,b,c,d,e See Table 9

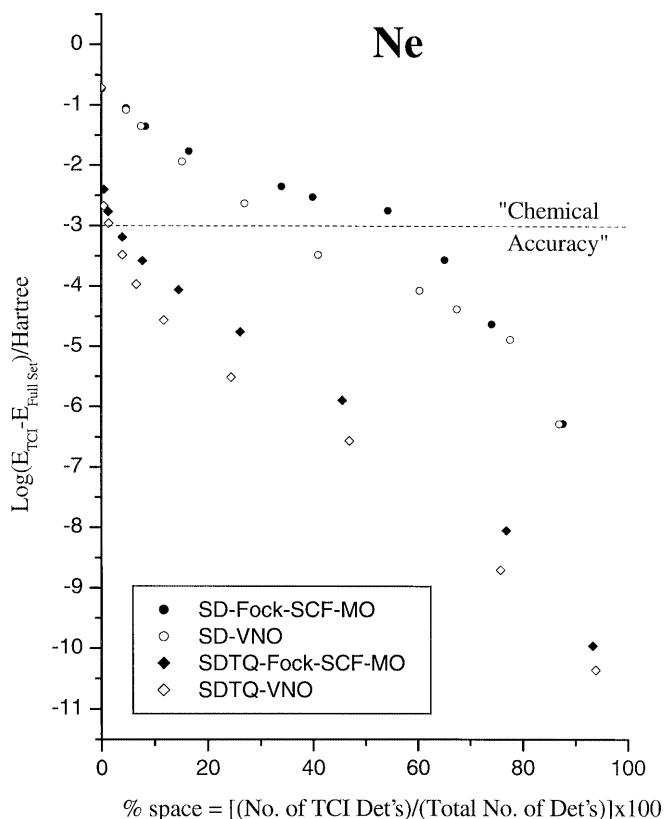


Fig. 1. Energy convergence of truncated singles+ doubles (*SD*) and singles+ doubles+ triples+ quadruples (*SDTQ*) configuration interaction (*CI*) expansions in terms of Fock-self-consistent-field (*SCF*) and virtual-natural-orbital (*VNO*)-based configurations for Ne. *TCI* represents truncated *CI*

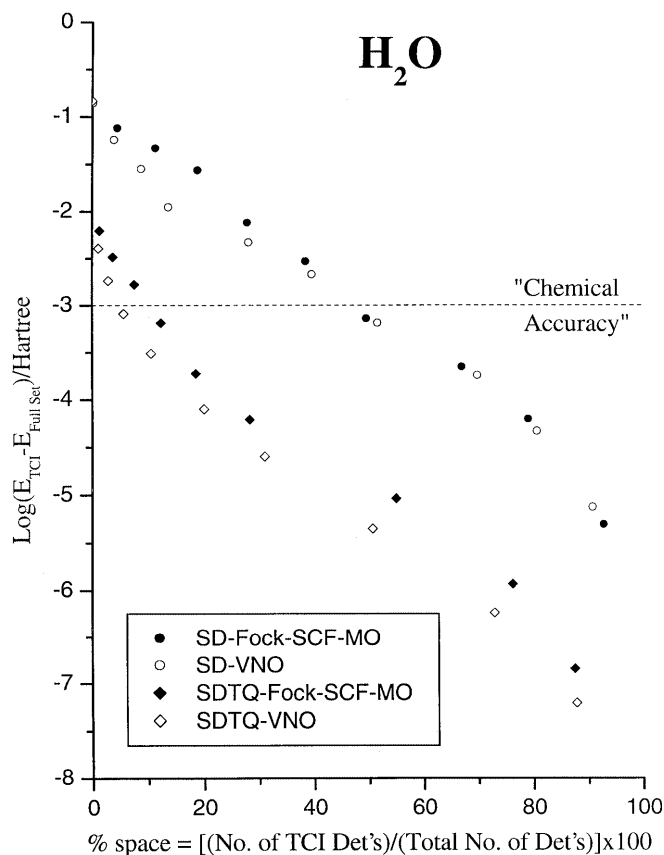


Fig. 2. Energy convergence of truncated *SD* and *SDTQ* *CI* expansions in terms of Fock-SCF and *VNO*-based configurations for H_2O

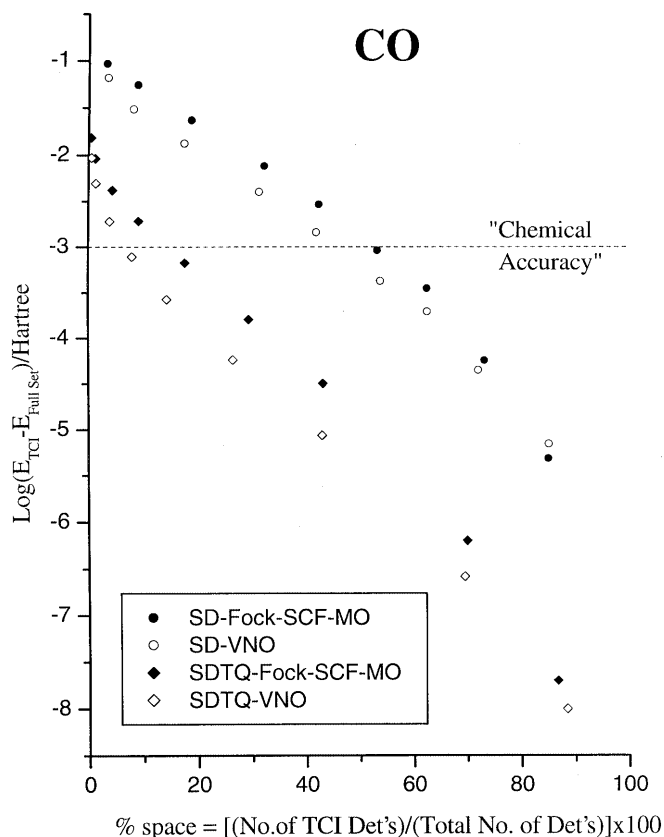


Fig. 3. Energy convergence of truncated SD and SDTQ CI expansions in terms of Fock-SCF and VNO-based configurations for CO

(equal to the number in the very first row of the same column of the table). The third and fourth rows of these sections furnish the analogous results obtained when the NOs in the virtual Fock space (VNOs) are used as correlating orbitals.

Discussion of SD expansions

The quantitative results of the truncations of SD wavefunctions are given in Tables 1, 3, 5 and 7. The implications are exhibited by the upper two curves in Figs. 1, 2, 3 and 4, which plot the decimal logarithm of the energy errors due to truncation, i.e. the fourth data columns in the tables, versus the truncation percentages, i.e. the second data columns in the tables. These curves exhibit the rates of convergence of the Fock-SCF-based (solid circles) and the VNO-based (open circles) SD expansions. Except for small regions in Figs. 1 and 2 where the curves are very close, it is seen that SD wavefunctions built from VNOs converge faster than those built from SCF orbitals, although the differences are not very large.

From the first sections of Tables 9, 10, 11 and 12 one can see that SD wavefunctions constructed from Fock-SCF orbitals (lines 3 and 4) recover 97, 95, 89 and 81% of the total correlation energy achievable by the basis set for Ne, H₂O, CO and C₂, respectively. (The lower percentage for C₂ is a result of the smaller basis set size

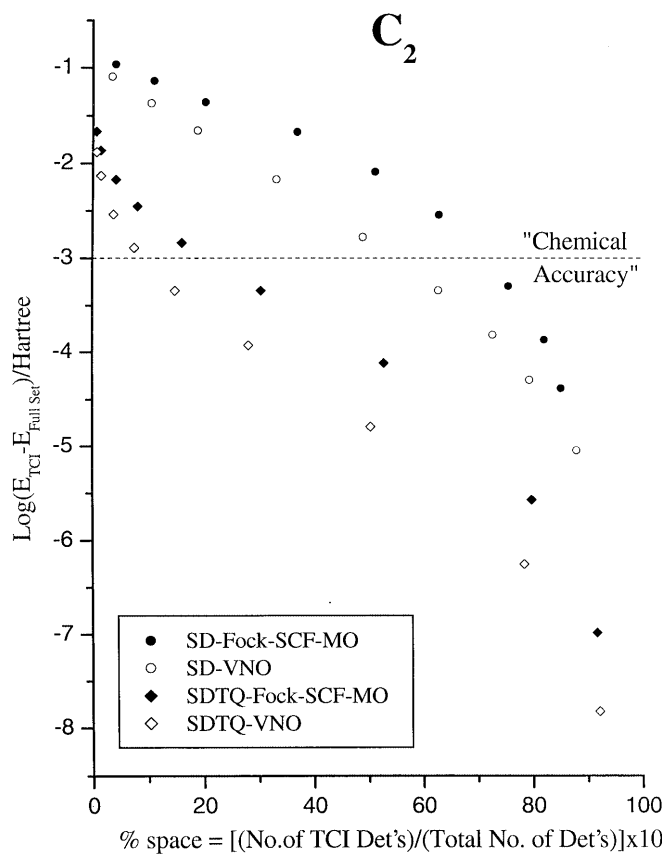


Fig. 4. Energy convergence of truncated SD and SDTQ CI expansions in terms of Fock-SCF and VNO-based configurations for C₂

yielding a SD space that is a smaller fraction of the full space.) For SD wavefunctions built using NOs of the total density matrix (lines 5 and 6), the percentage of the correlation energy recovered is seen to be always less than that for wavefunctions built from Fock-SCF orbitals but never by more than 1.4% (the difference for C₂).

The results given in the lower two sections of Tables 9, 10, 11 and 12 have been deduced from Figs. 1, 2, 3 and 4. Using VNOs, the truncation error in the energy is found to fall below 1 mhartree ("chemical accuracy") with approximately 34, 47, 46 and 55% of the full SD space for Ne, H₂O, CO and C₂, respectively. In order to fall below 0.1 mhartree, requires approximately 57, 75, 65 and 75% of the full SD space. The percentages are slightly higher when using the Fock virtual orbitals as correlating orbitals.

Discussion of SDTQ expansions

Tables 2, 4, 6 and 8 report the quantitative results of truncations of SDTQ wavefunctions. They are illustrated by the two lower curves in Figs. 1, 2, 3 and 4 which plot the SDTQ errors versus the truncation percentages. It is seen that the SDTQ wavefunctions constructed from VNOs (open circles) consistently converge more rapidly than those built from Fock-SCF orbitals (solid circles). The differences, although not large, are greater than those for the truncations of SD wavefunctions. It

should also be noted that, in all cases and for all orbital choices, the SDTQ errors decrease much more rapidly than the SD errors.

According to the first sections of Tables 9, 10, 11 and 12, the TQ contributions of the SDTQ wavefunctions built from Fock-SCF orbitals (lines 3 and 4) are 3, 5, 10 and 18% of the total correlation energy achievable within the limits of the basis sets for Ne, H₂O, CO and C₂, respectively. The third column shows that the quintuple and higher excitations contribute 0.1, 0.2, 1 and 2% of the full-space correlation energies and that the differences between the two orbital sets is less than 1 mhartree at this excitation level.

As with the SD cases, the data given in the lower two sections of Tables 9, 10, 11 and 12 have been deduced from Figs. 1, 2, 3 and 4. It is seen that, using VNOs, the truncation error in the energy falls below 1 mhartree with approximately 1, 4, 6 and 9% of the full TQ space for Ne, H₂O, CO and C₂, respectively. For the errors to fall below 0.1 mhartree requires approximately 6, 18, 22 and 31% of the full TQ space. These percentages, especially those for mhartree accuracy, are significantly less than the analogous percentages for the SD wavefunctions. As for the SD cases, they are higher when Fock virtual orbitals are used as correlating orbitals.

4 Conclusions

Using a previously described GCI code, CI calculations of truncated full-space determinantal expansions were performed to obtain qualitative assessments of the fractions of the SD and SDTQ wavefunctions that must be considered as deadwood with regard to correlation energy recovery. While the SD parts contain in no case more than 50% deadwood, the TQ parts typically contain an order of magnitude more deadwood than the SD parts. Expansions in terms of VNO-generated excitations converge somewhat faster than those gener-

ated directly from the virtual Fock-SCF orbitals. It will be of interest to see whether similar percentages will be found when larger atomic basis sets are used.

Acknowledgement. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under contract no. W-7405-Eng-82.

References

1. Ivancic J, Ruedenberg K (2001) *Theor Chem Acc* 106: 339
2. Saxe P, Schaefer HF III, Handy NC (1981) *Chem Phys Lett* 79: 202
3. Shavitt I, Rosenberg BJ, Palalikit S (1976) *Int J Quantum Chem Symp* 10: 33
4. (a) Bender CF, Davidson ER (1969) *Phys Rev* 183: 23; (b) Huron B, Rancurel P, Malrieu J-P (1973) *J Chem Phys* 58: 5745; (c) Buenker RJ, Peyerimhoff SD (1975) *Theor Chim Acta* 39: 217; (d) Buenker RJ, Peyerimhoff SD (1976) In: Löwdin PO, Pullman B (eds) *New horizons of quantum chemistry*. Reidel, New York, p 183; (e) Buenker RJ, Peyerimhoff SD, Butscher W (1978) *Mol Phys* 35: 771; (f) Pélissier M (1980) PhD thesis. Toulouse; (g) Evangelisti S, Daudey JP, Malrieu J-P (1983) *Chem Phys* 75: 91; (h) Buenker RJ (1986) *Int J Quantum Chem* 29: 435; (i) Feller D, Davidson ER (1989) *J Chem Phys* 90: 1024; (j) Knowles DB, Alvarez-Collado JR, Hirsch G, Buenker RJ (1990) *J Chem Phys* 92: 585; (k) Harrison RJ (1991) *J Chem Phys* 94: 5021; (l) Feller D (1993) *J Chem Phys* 98: 7059; (m) Krebs S, Buenker RJ (1995) *J Chem Phys* 103: 5613
5. See, e.g., Szabo A, Ostlund NS (1982) *Modern quantum chemistry*. Macmillan, New York
6. Koch H, Christiansen O, Jørgensen P, Olsen J (1995) *Chem Phys Lett* 244: 75
7. (a) Dunning TH Jr (1970) *J Chem Phys* 53: 2823; (b) Dunning TH Jr, P.J Hay (1977) In: Schaefer HF III (ed) *Methods of electronic structure*, vol 2. Plenum, New York, p.1
8. (a) Schmidt MW, Baldrige KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su SJ, Windus TL, Dupuis M, Montgomery JA (1993) *J Comput Chem* 14: 1347; (b) www.msg.ameslab.gov/GAMESS/GAMESS.html